

A LIFE CYCLE OF ORDERED WATER MOLECULES AT THE RuO_2 /WATER INTERFACE UNDER POTENTIAL CONTROL

This study examines the unique capability of undulator beams to investigate surface-sensitive phenomena on fuel cell electrodes. The study provides molecular-level details on two redox reactions and hydrogen and oxygen evolution reactions on the $\text{RuO}_2(110)$ surface under water. The investigation of liquid/solid interfaces using the Advanced Photon Source opens a new potential in this field.

By the year 2025, energy consumption is expected to reach an equivalent of 6 tons of coal per capita. By that time, pure hydrogen fuel, the ultimate form of renewable energy, is expected to meet approximately one-half of all energy consumption needs, and the world will enter the era of “hydrogen economy” [1]. This scenario, however, largely depends on the economical production of hydrogen and its conversion to electricity. The splitting of water (electrolysis) and the re-oxidation of hydrogen (fuel cells) occur at electrochemical interfaces, and a fundamental understanding of these processes is important for renewable energy development.

Conducting oxides (in particular ruthenium dioxide) are among the best electrodes for water electrolysis because of resistance to corrosion and insensitivity to impurities [2]. Ruthenium dioxide is also used in “supercapacitors” [3] because it produces an order of magnitude larger capacitance than the normal double layer due to surface redox processes. In a series of synchrotron x-ray studies, we determined a fascinating life cycle of oxygen atoms evolving from a hydrogen-bonded water layer, to an OH layer, and to a H_2O bilayer, and back to an OH and a water layer on a complete electro-

chemical cycle on the $\text{RuO}_2(110)$ surface [5]. We could achieve this because of the unprecedented level of sensitivity to monolayer and submonolayer oxygen atoms of our measurements, and a combination of the x-ray results with simple charge-balance and bond-length arguments. The structures determined provide previously unavailable molecular-level details of the redox processes and oxygen and hydrogen evolution reactions.

There are two charge-transfer reactions appearing in a voltammogram (I-V characteristics) of $\text{RuO}_2(110)$ surface measured in NaOH solution (Fig. 1a). The increase of the positive current at +600 mV

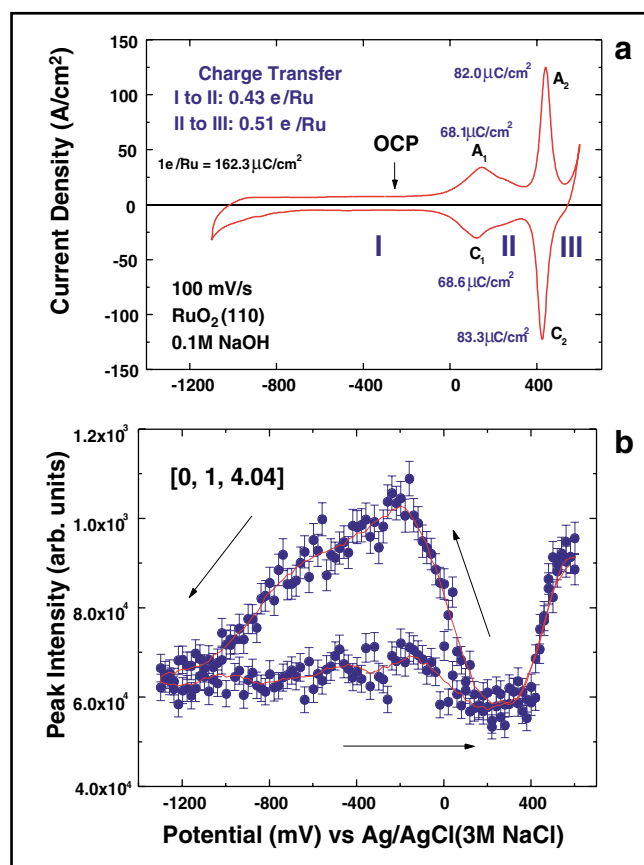


FIG. 1. Voltammogram (a) and x-ray intensity (b).

indicates oxygen evolution, and the increase of the negative current at -1100 mV indicates hydrogen evolution. The two pairs of reversible current peaks indicate two successive chemical transformations, and there are three surface oxidation states, denoted as I, II, and III, with their structures shown in Fig. 2. The Ru atoms are shown in blue, and the bulk oxygen atoms are shown in red. The oxygen atoms right above the Ru-O plane are shown in orange and those in the second layer in yellow. Since x-rays are insensitive to hydrogen, only oxygen positions were determined, and the species identification (i.e., O, OH, or H_2O) was based on structural (i.e., O-Ru bond length) and electrochemical (i.e., charge transfer, reaction mechanisms) considerations [5].

Structure II at 330 mV is the simplest. All Ru atoms are terminated with OH^- , and there are no dangling bonds. The surface maintains charge neutrality. OH^- ions are abundant in a basic solution to maintain the OH termination in thermodynamic equilibrium.

Reduction of the OH-terminated 330-mV structure at the C1 peak leads to structure I where every other row of OH is converted to water, which is trapped and anchored via hydrogen bonding between the remaining rows of OHs. In Fig. 1b, a large hysteresis loop of the x-ray intensity, approximately proportional to the height of the water molecules, is observable between 330 and -1200 mV. Although the water molecules are no longer strongly bonded to the Ru atoms at potential more negative than the C1 peak, they *remain* at their “birth” sites due to the still remaining attraction of the oxygen of water to Ru atoms. As the potential decreases from the C1 peak, the height of oxygen atoms of the commensurate water increases. Around -300 mV, however, the height of the water molecules reaches a maximum where the water molecules are least attracted to the surface. As the potential is swept negative, the reorientation of water molecules due to the attraction of hydrogen atoms to the surface leads to the destruction of the hydrogen bonds stabilizing the water monolayer. Eventually, the commensurate water network disappears below -1000 mV. At this potential, the hydrogen of water molecules is

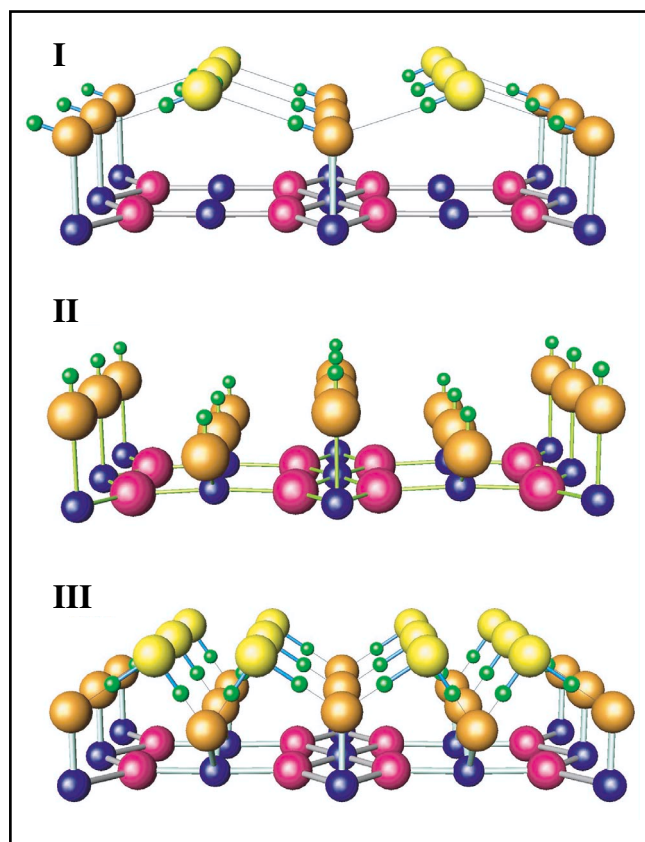


FIG. 2. The structures for three oxidation states.

adsorbed on the surface, and a slightly lower potential allows the water molecules to split, resulting in H_2 evolution. A reversal of the polarity does not restore the lost hydrogen network and commensurability until the potential reaches that of A1 peak where OH is chemisorbed to Ru atoms.

The oxidation of structure II at A2 peak leads to the 500-mV bilayer structure: the lateral water-water distances are essentially locked to the underlying lattice, but the interlayer separation is much smaller than typical oxygen-oxygen distances in ordinary forms of water or ice because the outer layer is under the extremely high interfacial electric field (10^9 to $\sim 10^{10}$ V/m) [5]. When the O-H \cdots O bond length is in the range from 2.2 to 2.4 Å, as it is in this case, the hydrogen is centered between two oxygen atoms in an effective single-well potential, like in ice X [6]. At slightly higher potentials, the centered hydrogen atoms are likely to escape, allowing the oxygen atoms to bond directly, resulting in O_2 evolution.

Our study provided molecular-level details on two redox reactions and hydrogen and oxygen evolution reactions on the RuO₂(110) surface under water. Such molecular-level studies were only possible due to the availability of extremely powerful synchrotron x-rays, so that one could obtain extremely high signal-to-noise ratios and utilize advanced x-ray techniques that are sensitive to light elements such as oxygen. Liquid/solid interfaces are, in general, an underexplored area of science due to experimental difficulties, but the use of synchrotron techniques promises fruitful future results.

We thank the staff at the Basic Energy Science Synchrotron Radiation Center for their assistance during the experiments at 12-ID-B and 12-BM-B. This work was supported by the U.S. Department of Energy, Office of Science, Office of Basic

Energy Sciences, Chemical Sciences Division, under Contract No. W-31-109-ENG-38.

Principal publication: “Commensurate Water Monolayer at the RuO₂ (110)/Water Interface,” *Phys. Rev. Lett.* **86**, 3364-3367 (2001).

REFERENCES:

- [1] J.H. Ausubel, *Industrial Physicist* **6**, 16 (2000).
- [2] S. Trasatti and G. Lodi, in *Electrodes of Conductive Metal Oxides, Part B*, edited by S. Trasatti (Elsevier, Amsterdam, 1991), p. 521.
- [3] B.E. Conway, *J. Electrochem. Soc.* **138**, 1539-1548 (1991).
- [4] Y.S. Chu, T.E. Lister, W.G. Cullen, H. You, and Z. Nagy, *Phys. Rev. Lett.* **86**, 3364 (2001).
- [5] For doubly charged oxygen, the electrostatic force on a square meter of water molecules with an average distance of 2.4 Å is approximately 5 to ~50 GPa, which is similar to the pressure for ice X.
- [6] M. Benoit, D. Marx, and M. Parrinello, *Nature* **392**, 258-261 (1998).

T. E. Lister,¹ Y. S. Chu,² W. G. Cullen,¹ Z. Nagy,¹ H. You¹

¹Materials Science and ²Experimental Facility divisions, Argonne National Laboratory, Argonne, IL, U.S.A.